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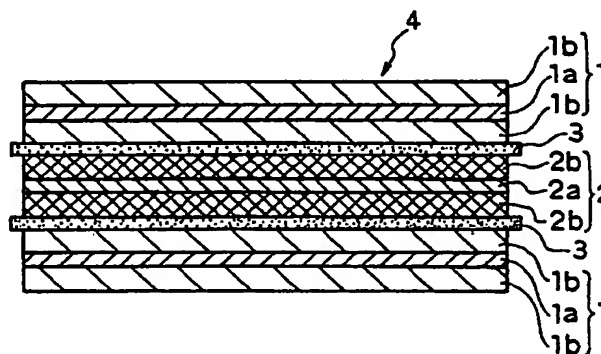
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(54) **Polymer electrolyte battery**

(57) Disclosed is a polymer electrolyte battery affording a high capacity density in which a layer of electrode active material mixture containing a polymer has an adequately regulated porosity and/or polymer content. The battery includes a unitary laminated battery sheet composed of a negative electrode combined with positive electrodes, with a porous polymer separator being placed on both surfaces of the negative electrode. Each of the electrodes comprises a current collector and a layer of active material mixture disposed on both surfaces of the current collector, and the polymer is capable of absorbing and retaining nonaqueous electrolyte. The separator and the layer of electrode active material mixture have a porosity of 30 to 60%. Preferable polymer contents in the layer of active material mixture are in a range of 5 to 10 wt% for the positive electrode and in a range of 7 to 16 wt% for the negative electrode.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

5 [0001] The present invention relates to a polymer electrolyte battery, particularly to a flat polymer electrolyte battery comprising a thermally unitary laminated structure composed of electrode films or sheets and separator films or sheets, the electrodes and separators containing a polymer capable of absorbing and retaining a nonaqueous electrolyte.

[0002] With the recent development of compact, thin and lightweight portable appliances, there has been a strong demand for a compact, thin and lightweight battery as a power source therefor. Lightweight lithium ion batteries afford-
 10 ing a high energy density have already been realized, much contributing to down-sizing and weight reduction of portable phones and portable personal computers. However, there is still an ever-increasing serious demand for further minimized lightweight portable appliances. However, conventional lithium ion batteries realizing a short distance between positive and negative electrodes and a satisfactory contact between the electrode and a separator by tightly securing a laminate of the positive and negative electrodes and the separator inside a rigid and firm metal jacket case
 15 have the following drawback: A certain thickness is required for the metal jacket case in order to secure its strength, which limits realization of a thinner lithium ion battery.

[0003] One noted method for realizing a thin lithium ion battery is lithium polymer secondary batteries including a poly-
 20 meric material as the electrolyte. Among them, a battery system wherein an electrolyte layer and electrodes are unitary bound to each other is effective in realizing a thin battery system, because it can provide a satisfactory contact between the electrolyte layer and the electrodes without need of the above-mentioned rigid and firm metal jacket case. Examples of a battery comprising a unitary bound structure of an electrolyte layer and electrodes can be found in the U.S. Patents No. 4,830,939 and 5,478,668.

[0004] The U.S. Patent No. 4,830,939 discloses a lithium battery wherein a mixed solution of a monomer and an elec-
 25 trolyte is applied onto the negative electrode made of metallic lithium or the positive electrode, which is then irradiated with ultraviolet ray or electron beam to polymerize the monomer and eventually form a solid polymer electrolyte. Since the layer of the electrolyte is formed along the fine uneven surface of the electrode, the contact between the electrode and the electrolyte layer becomes satisfactory without securing the one to the other.

[0005] The U.S. Patent No. 5,478,668, on the other hand, discloses a copolymer (hereinafter referred to as
 30 "P(VDF/HFP)" of vinylidene fluoride (hereinafter referred to as "VDF") and hexafluoropropylene (hereinafter referred to as "HFP") as a polymer material. A positive electrode, a negative electrode and a polymer separator are formed first and then the separator is unitary laminated to the positive or the negative electrode.

[0006] The use of such unitary bound sheet-like structure of an electrode and an electrolyte layer as the power gen-
 erating element as disclosed in the above-mentioned two U.S. patents can give a thin rechargeable battery even when it is housed in a jacket case of a thin and flexible laminate sheet.

35 [0007] In order to obtain a battery which can give an operational battery capacity, this type of battery was initially formed in multiplexed-cell structure by simply piling a multiplicity of cells, each cell being formed, using a pair of positive and negative current collectors, by placing a positive electrode sheet and a negative electrode sheet to face each other, with a polymer separator being placed therebetween. The positive electrode sheet comprises a current collector and a layer of positive active material mixture disposed on one surface of current collector and the negative electrode sheet
 40 comprises a current collector and a layer of negative active material mixture disposed on one surface of the current collector. This structure, however, produces a drawback that the surface of current collector not in contact with the active material mixture fails to participate in the event of discharge, which in turn increases the percentage of the current collectors in the battery volume, compared to the conventional lithium ion battery.

[0008] In order to solve the above-mentioned problems, there is a recently proposed structure of a battery in the Jap-
 45 anese Laid-Open Patent Publication Hei 10-189053 such that a negative electrode whose porous current collector has a layer of negative active material mixture on both surfaces is sandwiched between positive electrodes whose porous current collector has a layer of positive active material mixture on one surface or both surfaces, with a polymer separator interposed therebetween. This structure facilitates realization of a thin and lightweight battery of high energy density while retaining satisfactory characteristics as a battery.

50 [0009] Specific production process of such polymer electrolyte battery is shown below:

[0010] First, a paste is prepared from a mixture of an electrode active material powder and a conductive agent powder added with an organic solvent solution of a polymer and dibutyl phthalate as a pore forming material. The resultant
 55 paste is applied onto both surfaces of a porous current collector for the negative electrode and one or both surfaces of another porous current collector for the positive electrode. Those two electrode sheets are then dried to evaporate the organic solvent, which gives a positive electrode sheet and a negative electrode sheet. The positive and negative electrode sheets thus obtained and polymer separator sheets containing a pore forming material are laminated alternately in the order of positive electrode sheet, separator, negative electrode sheet, separator and positive electrode sheet. The resultant laminate is pressed under heat, which gives a unitary laminated sheet for use as a battery element. The bat-

tery element sheet is then immersed in, for example, an extracting solvent diethyl ether for removing the pore forming material from the sheet. After the battery element sheet becomes enough porous and have pores by this treatment, a nonaqueous electrolyte is allowed to impregnate into the pores of the electrode sheet and the polymer separator sheet.

[0011] In the polymer electrolyte battery thus obtained, the capacity density depends on the porosity and the ratio of polymer of the electrodes. This means that if the loading or packing density of electrode active material is increased by rolling the electrode sheet after applying the above-noted paste onto the current collector to reduce the degree of porosity, the electrolyte would not enter the electrode sufficiently. As a result, the utilization of electrode active material decreases. To the contrary, if the total spatial volume inside the electrode is increased by lowering the loading density of electrode active material and the porosity is increased, the electrolyte enters the electrode sufficiently. This increases the utilization of electrode active material but reduces the absolute volume of active material. Higher percentages of polymer in the electrode result in relative reductions of the volume of active material and lower percentages result in impaired electrode strength. When the percentage of polymer in the electrode is high, the polymer becomes rubbery upon stirring to make it into paste, which disturbs sufficient rolling of the electrode. Furthermore, the use of a lathe sheet as the porous current collector may not increase the loading density of electrode active material, because the current collector is stretched together with the electrode active material mixture and is even torn or pulled off during rolling. To the contrary, a low percentage of polymer in the paste interferes with thermally unitary laminating the electrode sheets and separators, forming a gap between the electrode and the separator and elevating the internal resistance of the resultant battery. Therefore, stable performance cannot be expected for such battery. Based on the above considerations, the adequate percentage of polymer in the layer of electrode active material mixture has been conventionally 20 wt% or so.

BRIEF SUMMARY OF THE INVENTION

[0012] In view of the above-mentioned problems, the object of the present invention is to provide a thin and lightweight polymer electrolyte battery of high capacity density by optimizing the porosity of electrode sheet using a certain range of concentration of polymer in the layer of electrode active material mixture and/or by optimizing the polymer content by regulating to a fixed extent rolling operation for adjusting the porosity of electrode sheet, thereby increasing the loading density of electrode active material mixture.

[0013] The present invention provides a polymer electrolyte battery including:

a nonaqueous electrolyte,
positive and negative electrode films or sheets each of which comprises a porous current collector and a layer of active material mixture disposed on both surfaces of the porous current collector, the layer of active material mixture containing a polymer capable of absorbing and retaining the electrolyte, and
porous separator films of a polymer capable of absorbing and retaining the electrolyte, the electrolyte being retained in the positive and negative electrodes and the separators,
wherein the positive electrodes are unitary laminated on the negative electrode with the separator being placed on both surfaces of the negative electrode to form a unitary laminated battery element sheet, and wherein the separator and the layer of active material mixture of the positive and negative electrodes have a porosity in a range of 30 to 60%.

[0014] For this battery, a preferred porosity of the layer of active material mixture is in a range of 35 to 55% for the positive electrode and in a range of 35 to 45% for the negative electrode. A preferred porosity of the separator is in a range of 50 to 55%.

[0015] The porosity of the layer of active material mixture is represented as follows:

$$\frac{(\text{Total spatial volume of the layer of active material mixture})}{(\text{total volume of the layer of active material mixture})} \times 100 (\%)$$

[0016] The present invention also provides a polymer electrolyte battery comprising a nonaqueous electrolyte, positive and negative electrode films or sheets whose porous current collector has a layer of active material mixture containing a polymer on both surfaces, and porous separators of a polymer, each polymer being capable of absorbing and retaining the electrolyte, the electrolyte being retained in the positive and negative electrodes and the separators, wherein the positive electrodes are opposed to the negative electrode with the separator being placed on both surfaces of the negative electrode to form a unitary laminated battery element sheet, and wherein the layer of active material mixture contains the polymer in a range of 5 to 10 wt% for the positive electrode and in a range of 7 to 16 wt% for the negative electrode.

[0017] For this battery, it is more preferable that the layer of active material mixture contains the polymer in a range of 6 to 8 wt% for the positive electrode and in a range of 8 to 15% for the negative electrode.

[0018] The present invention provides a further polymer electrolyte battery whose polymer content in the layer of active material mixture is in a range of 5 to 10 wt% for the positive electrode and in a range of 7 to 16 wt% for the negative electrode and whose separator and layer of active material mixture have a porosity in a range of 35 to 55%.

[0019] For this battery, it is preferable that the layer of active material mixture has a porosity in a range of 35 to 55% for the positive electrode and a porosity in a range of 35 to 45% for the negative electrode, and contains the polymer in a range of 6 to 8 wt% for the positive electrode and in a range of 8 to 15 wt% for the negative electrode.

[0020] While the novel features of the invention are set forth particularly in the appended claims, the invention, both as to organization and content, will be better understood and appreciated, along with other objects and features thereof, from the following detailed description taken in conjunction with the drawings.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

[0021]

FIG. 1 is a diagrammatic longitudinal cross-sectional sketch showing a battery element of a polymer electrolyte battery in accordance with the present invention.

FIG. 2 is a graph illustrating changes in discharge capacity observed in polymer electrolyte batteries in accordance with the present invention which have different porosity for the layer of positive active material mixture and constant porosity for the layer of negative active material mixture.

FIG. 3 is a graph illustrating changes in discharge capacity observed in polymer electrolyte batteries in accordance with the present invention which have different porosity for the layer of negative active material mixture and constant porosity for the layer of positive active material mixture.

FIG. 4 is a graph illustrating the relationship between the discharge rate and discharge capacity observed in batteries with different porosity for the layer of positive active material mixture.

FIG. 5 is a graph illustrating the relationship between the discharge rate and discharge capacity observed in batteries with different porosity for the layer of negative active material mixture.

FIG. 6 is a graph illustrating the relationship between the polymer content and loading density of active material mixture in the positive electrode.

FIG. 7 is a graph illustrating the relationship between the polymer content and loading density of active material mixture in the negative electrode.

FIG. 8 is a graph illustrating the relationship between the thickness and elongation (stretch) rate of electrode sheet observed at production of positive electrodes with different polymer contents.

FIG. 9 is a graph illustrating the relationship between the thickness and elongation (stretch) rate of electrode sheet observed at production of negative electrodes with different polymer contents.

FIG. 10 is a graph illustrating the relationship between the polymer content in the positive electrode and discharge capacity of the resultant battery.

FIG. 11 is a graph illustrating the relationship between the polymer content in the negative electrode and discharge capacity of the resultant battery.

FIG. 12 is a graph illustrating the relationship between the polymer content in the positive electrode and internal resistance in the resultant battery.

FIG. 13 is a graph illustrating the relationship between the polymer content in the negative electrode and internal resistance in the resultant battery.

DETAILED DESCRIPTION OF THE INVENTION

[0022] An example of the polymer electrolyte battery in accordance with the present invention will be described with reference to FIG. 1.

[0023] A positive electrode sheet 1 is produced as follows: First, a paste of a positive active material mixture is prepared by mixing and kneading an organic solvent solution of a polymer and a compatible plasticizer for the polymer as a pore forming material with a mixture of a powder of a positive active material and a powder of a conductive agent. The resultant paste is applied onto both surfaces of a porous current collector 1a and dried to form a layer of positive active material mixture 1b. Then, the collector 1a is rolled with a pressure roller and cut into a sheet of a predetermined size. Next, a negative electrode sheet 2 is produced as follows: A paste of a negative active material mixture is prepared by mixing and kneading an organic solvent solution of a polymer and a compatible plasticizer for the polymer as a pore forming material with a mixture of a powder of a negative active material and a powder of a conductive agent. The resultant paste is applied onto both surfaces of a porous current collector 2a and dried to form a layer of negative active

material mixture 2b. Then, the collector is rolled with a pressure roller and cut into a sheet of a predetermined size. In this way, electrode films or sheets with a thickness of 250 to 450 μm can be produced. A separator 3 is a polymer sheet with a thickness of 20 to 70 μm containing a compatible plasticizer for the polymer as a pore forming material. Each of the layer of active material mixture 2b on the negative electrode sheet 2 is opposed to the layer of active material mixture 1b on the positive electrode sheet 1 with a separator being placed therebetween and formed into a laminated sheet. The laminated sheet is then heat-treated to form a unitary laminated battery element sheet 4. The pore forming material is then extracted to make the polymer porous in order to form a number of pores into which an electrolyte can be permeated. When 2 or more pieces of battery element sheet 4 are laminated, a polymer electrolyte battery affording a desired capacity can be obtained.

[0024] When a polymer electrolyte battery is produced in the above-mentioned process, it is preferable to regulate the porosity of the layer of electrode active material mixture by the degree of rolling treatment with a pressure roller. Another method for regulating the porosity of the layer of electrode active material mixture is to control the ratio of the pore forming material to the polymer. The porosity, which is dependent on the amount of pore forming material, is necessary for permeating and retaining the electrolyte in the battery element. If the ratio of the polymer to the electrode active material is fixed, the ratio of the pore forming material to the polymer is also fixed.

[0025] As such, there are two supposed methods for regulating the porosity: (1) Regulation by the degree of rolling with a pressure roller and (2) Regulation by the ratio of the pore forming material. In the method (1), rolling in greater degrees deforms or destroys polymer particles. As a result, the pores formed after removal of pore forming material have only small sizes and the overall porosity becomes small. To the contrary, rolling in lesser degrees may not deform or destroy polymer particles. As a result, the pores formed after removal of pore forming material have large sizes and the overall porosity becomes large. In the method (2), on the other hand, smaller ratios of the pore forming material form only a small number of pores, decreasing the overall porosity. Greater ratios form a great number of pores, increasing the overall porosity. In fact, the porosity is determined by regulating both the degree of rolling and the ratio of the pore forming material. In either case, if the obtained electrode sheet has a small porosity, permeation of the electrolyte into the electrode becomes insufficient, reducing the discharge capacity particularly at high-rate discharge. On the other hand, if the obtained electrode sheet has a large porosity, it increases in thickness when it is loaded with an active material in the same amount. This results in a longer distance between the discharge side of the electrode and the current collector, reducing the discharge capacity. Moreover, since such electrode may be increased in volume, volume efficiency also decreases. If the thickness is the same, the relative ratio of the active material decreases, rendering the absolute battery discharge capacity smaller. Furthermore, excess porosity reduces the mechanical strength of the electrode sheet, leading to impaired cycle characteristics as a battery.

[0026] The present invention is based on the discovery of an optimal range of porosity for the layer of active material mixture and for the separator from an experiment to regulate the degree of rolling in producing the layer of active material mixture and the separator using a constant polymer content and a constant ratio of the pore forming material, considering that the number and size of pores which are determinants of porosity are dependent on the two factors (1) amount of the pore forming material and (2) loading density in the layer of active material mixture.

[0027] In order to have a battery affording a large capacity density, it is preferable for the layer of electrode active material mixture to have a smallest polymer content. Larger polymer contents produce various inconveniences such that the electrode active material mixture becomes rubbery, hindering sufficient rolling of the electrode, or current collector is rolled together with the active material mixture and torn off. On the other hand, smaller polymer contents disturb binding by heating the electrode film or sheet to the separator to form a unitary laminated sheet, producing a gap between the electrode and the separator. A battery including such an element sheet is increased in internal resistance and fails to exhibit stable performance.

[0028] The present inventions is also based on another discovery of an optimal range of the polymer content in the layer of active material mixture of the positive and negative electrodes from an experiment to reduce the polymer content in the layer of electrode active material mixture compared to conventionally used contents in order to find optimal conditions for binding by heating the electrode and the separator into a unitary laminated sheet and realize stable battery performance. It must be noticed that the amount of the electrolyte was ignored in calculating polymer content.

[0029] In the above-mentioned method for producing the polymer electrolyte battery in accordance with the present invention, an optimal polymer content was determined from the values of loading capacity observed in the electrodes produced by varying polymer contents but fixing the amount of the active material mixture constituting an electrode and the polymer/pore forming material ratio, and the values of discharge capacity and internal resistance observed in the batteries including such electrodes. In this case, the weight ratio of the pore forming material to the polymer is preferably in a range of 1 to 2.

[0030] According to the present invention, a polymer electrolyte battery of further greater capacity density can be obtained with the use of an electrode whose polymer content and porosity have been optimized, because performance of the above-mentioned electrode and battery is largely affected by the two factors, porosity and polymer content in the layer of the electrode active material mixture.

[0031] In the present invention, although a copolymer of VDF and HFP, that is, P(VDF/HFP), is a preferred polymer for use in the electrode and separator, the polymer is not limited to such copolymer, and any of polymers which can absorb and retain a nonaqueous electrolyte and can work as a binder for binding an active material to the current collector and for binding electrode sheets and separator sheets to each other is also applicable. In the present invention, the pore forming material is not limited to dibutyl phthalate.

[0032] The polymer electrolyte used in the present invention is the so-called solid polymer electrolyte, particularly gel-type solid polymer electrolyte. Details of applicable polymer, plasticizer and nonaqueous electrolyte can be found in the U.S. Patent No. 5,418,091 and the above-mentioned U.S. Patent No. 5,478,668 (which are incorporated herein by reference in their entirety).

[0033] As the positive active material, a compound such as LiCoO_2 , LiNiO_2 or LiMn_2O_4 that can reversibly intercalate and deintercalate lithium upon discharge and charge, particularly a lithiated transition metal oxide is used.

[0034] As the negative active material, a carbon material or something like that is used which can reversibly intercalate and deintercalate lithium upon charge and discharge. Graphite is a particularly desired material in order to obtain a high capacity battery. A preferred graphite material is a spheric graphite powder with a mean particle size of 6 to 50 μm prepared by carbonizing and graphitizing a carbonaceous mesophase particle. A more preferred material is a spheric graphite powder in which the interplanar spacing is 3.365 to 3.390 angstroms and the crystal size is 200 to 650 angstroms along the c axis by X-ray diffractometry, and the I_{1360}/I_{1580} ratio of the peak intensity I_{1360} at 1360 cm^{-1} to the peak intensity I_{1580} at 1580 cm^{-1} by argon laser-Raman spectrometry is in a range of 0.20 to 0.40.

[0035] As the positive current collector, a perforated plate, lathe sheet or net of aluminum, titanium, stainless steel or the like, or something like that is used. As the negative current collector, a perforated plate, lathe sheet or net of copper, stainless steel or the like, or something like that is used. When the polymer electrolyte battery is formed to have the multiplexed-cell structure as mentioned before, it is preferable to use a perforated porous sheet having non-perforated margin for the electrodes, in consideration of subsequent attachment of the respective lead terminal.

[0036] The nonaqueous electrolyte may be one arbitrarily selected from among various conventionally known combinations for use in polymer electrolyte battery, for example, a combination of a solute, such as LiClO_4 , LiBF_4 , LiPF_6 , LiCF_3SO_3 or the like with a solvent, such as ethylene carbonate, propylene carbonate, ethyl methyl carbonate, dimethoxyethane or the like.

[0037] In a preferred mode of the present invention, the polymer should be a VDF/HFP copolymer (P(VDF/HFP) and the electrode active material should contain a carbonaceous conductive agent such as carbon black and have a polymer content in a range of 5 to 16 wt% and a porosity in a range of 30 to 60%. In consideration of battery characteristics, particularly charge/discharge cycle life characteristic, the polymer content in the positive active material mixture is more preferably in a range of 5 to 10 wt% and the porosity is more preferably in a range of 35 to 55% when an oxide as exemplified above is employed as the positive active material. On the other hand, it is more preferable for the negative active material mixture to contain the polymer in a range of 7 to 16 wt% and have a porosity in a range of 35 to 45% when it includes the above-noted spheric graphite powder.

[0038] In the following, the present invention will be described more specifically by way of concrete examples.

Example 1

[0039] 100 g of P(VDF/HFP) (HFP ratio = 12 wt%) and 50 g of silica powder (SiO_2) were mixed in 500 g acetone to produce a silica-dispersed solution. To the resultant solution, 150 g of dibutyl phthalate (hereinafter referred to as "DBP") was added and dissolved. The silica-dispersed solution containing DBP was applied onto a glass plate and dried to evaporate acetone, which gave a separator film of 300 μm thick. The film was cut into a separator sheet of 40 mm \times 60 mm.

[0040] Separately, 90 g of P(VDF/HFP) was dissolved in 1,500 g acetone into which 900 g of LiCoO_2 , 50 g of acetylene black and 135 g of DBP were mixed and kneaded to make a paste. The paste thus obtained was applied onto both surfaces of an aluminum lathe sheet of 40 μm thick serving as a positive current collector and dried. The dried sheet was then rolled under pressure to produce a positive electrode sheet of 100 μm thick. The sheet was then cut into a sheet of 35 mm \times 55 mm for use as the positive electrode.

[0041] Similarly, 120 g of P(VDF/HFP) was dissolved in 1,000 g acetone into which 750 g of a spheric graphite powder with a mean particle size of 20 μm (manufactured by Osaka Gas Co. Ltd., Osaka, Japan) prepared by carbonizing and graphitizing a carbonaceous mesophase particle, 60 g of a graphite fiber as a conductive agent (manufactured by Osaka Gas Co. Ltd., Osaka, Japan), and 180 g of DBP were mixed and kneaded to make a paste. The graphite fiber was prepared by graphitizing a carbon fiber obtained by vapor phase epitaxy. The paste thus obtained was applied onto both surfaces of a copper lathe sheet of 50 μm thick serving as a negative current collector and dried. The dried sheet was then rolled under pressure to produce a negative electrode sheet of 300 μm thick. The sheet was then cut into a sheet of 35 mm \times 55 mm for use as the negative electrode.

[0042] The positive and negative current collectors used in the present invention were preformed on the respective

surfaces with a conductive carbon coating film. The film was formed by applying a dispersion of acetylene black in a 12 wt% N-methyl-2-pyrrolidone solution of polyvinylidene fluoride and drying the resultant at 80 °C or more.

[0043] The negative electrode sheet thus obtained was disposed on both surfaces with the positive electrode sheet, with the separator film being placed therebetween. The resultant combination was passed through a pair of pressure rollers preheated to 150 °C to press and bind it into a unitary laminated sheet for use as a battery element. The battery element sheet was then immersed in an extracting solvent diethyl ether to remove DBP and make the polymer porous. The resultant porous sheet was dried in a vacuum at 50 °C and immersed in an electrolyte under reduced pressure for predetermined hours to permeate the electrolyte into the pores and the polymer inside the electrodes and the separator. The electrolyte used here is 1 mol/l LiPF₆ in a solvent mixture of ethylene carbonate and ethyl methyl carbonate at a volumetric ratio of 1 : 3.

[0044] The battery element sheet thus obtained was mounted with a laminate film prepared by inserting an aluminum film between two resin films which gave a battery of 0.6 mm thick and 40 mm × 60 mm.

[0045] In this battery, the porosity was 45% in the layer of active material mixture of the positive electrode, 40% in that of the negative electrode, and 53% in the separator. The polymer content excluding the amount of electrolyte was 8.7 wt% in the layer of active material mixture of the positive electrode, 12.9 wt% in that of the negative electrode, and 66 wt% in the separator. Although the above-mentioned separator has a porosity of 53%, a preferable separator has a porosity in a range of 50 to 55% in consideration of electrolyte retention and ionic conductivity of the resultant battery.

[0046] Next, batteries 1 to 7 with a fixed porosity of 40% for the layer of negative active material mixture and different porosities for the layer of positive active material mixture were produced. For comparison, batteries 8 to 14 with a fixed porosity of 45% for the layer of positive active material mixture and different porosities for the layer of negative active material mixture were also produced. Table 1 lists the porosity of the positive and negative electrodes in those 14 battery samples.

Table 1

Battery sample	Porosity of positive electrode (%)	Porosity of negative electrode (%)
Battery 1	25	40
Battery 2	35	40
Battery 3	40	40
Battery 4	45	40
Battery 5	50	40
Battery 6	55	40
Battery 7	70	40
Battery 8	45	23
Battery 9	45	30
Battery 10	45	35
Battery 11	45	40
Battery 12	45	45
Battery 13	45	52
Battery 14	45	65

[0047] The batteries were compared for their battery characteristics in the following manner and the results will be described.

[0048] First, batteries 1 to 7 were discharged at a rate of 0.2 C until the terminal voltage decreased to 3.0 V to determine the discharge capacity of each battery which results are shown in FIG. 2. In the figure, abscissa represents the porosity in the layer of positive active material mixture in each battery. Batteries 8 to 14 were tested similarly and the results are shown in FIG. 3.

[0049] As evident from the data shown in the two figures, the battery discharge capacity varies greatly by the porosity of the layer of active material mixture despite the use of the same amount of the active material.

[0050] Positive and negative electrodes having a porosity in the range of 30 to 60% can give a satisfactory capacity

characteristic to the respective batteries including those electrodes. More particularly, positive electrodes having a porosity of 35 to 55% and negative electrodes having a porosity of 35 to 45% can produce a capacity of 80 mAh (corresponding to active material utilization 80%) or more, and thus are more preferable.

[0051] Then, batteries 1, 3 and 6 in the former group and batteries 8, 11 and 13 in the latter group were discharged at different discharge rates. FIG. 4 shows the relationship between the discharge rate and discharge capacity in batteries 1, 3 and 6 with different porosity for the positive electrode. FIG. 5 shows the relationship between the discharge rate and discharge capacity in batteries 8, 11 and 13 with different porosity for the negative electrode. These figures clearly indicate that batteries including an electrode active material with inadequate porosity can not produce a discharge capacity in correspondence with the loaded amount of the active material irrespective of discharge rate.

Example 2

[0052] Following the procedure in Example 1, positive electrodes 15 to 23 were produced, except that polymer (P(VDF/HFP)) content in the layer of positive active material mixture was changed, and batteries 15 to 23 including the resultant electrodes 15 to 23 were produced. Similarly, negative electrodes 24 to 33 were produced, except that polymer (P(VDF/HFP)) content in the layer of negative active material mixture was changed, and batteries 24 to 33 including the resultant electrodes 24 to 33 were produced. Tables 2 and 3 list the polymer contents in the battery samples 15 to 33 thus obtained. In producing batteries of Example 2, the ratio of DBP to the polymer P(VDF/HFP) was fixed at 1.5.

Table 2

Battery sample	Polymer content in positive electrode (wt%)
Battery 15	2
Battery 16	4
Battery 17	5
Battery 18	6
Battery 19	7
Battery 20	8
Battery 21	10
Battery 22	15
Battery 23	25

Table 3

Battery sample	Polymer content in negative electrode (wt%)
Battery 24	5
Battery 25	6
Battery 26	7
Battery 27	8
Battery 28	9
Battery 29	10
Battery 30	12
Battery 31	15
Battery 32	16

Table 3 (continued)

Battery sample	Polymer content in negative electrode (wt%)
Battery 33	25

[0053] The electrodes and the batteries thus produced were compared for their characteristics, and the results will be described.

[0054] First, the relationship between the polymer content in the layer of the active material mixture and loading density of the active material in the positive electrode is shown in FIG. 6 and the relationship between the polymer content in the layer of the active material mixture and loading density of the active material in the negative electrode is shown in FIG. 7.

[0055] FIG. 8 and FIG. 9 respectively illustrate the elongation (stretch) rate of electrode sheet during rolling under pressure at production of positive electrodes 15 to 23 and negative electrode 24 to 33.

[0056] As apparent from the two graphs, the positive and negative electrodes decrease in loading density in the layer of the active material mixture with increases in polymer content. Increased polymer content enhances elongation rate of the sheet upon rolling the electrode under pressure. When electrode sheets are pressed to increase their active material loading density, the polymer in the sheets may manifest its intrinsic rubbery property in excess if the polymer content is too high, elongating the current collector before it is formed into a thin electrode sheet by sufficiently pressing the layer of the active material mixture. Therefore, excess polymer content disturbs production of thin electrodes and thus lowers the loading density of the active material. The resultant battery, therefore, cannot have expected high capacity.

[0057] FIG. 10 illustrates discharge capacities in batteries 15 to 23 obtained in a test to discharge at a rate of 0.2 C until the terminal voltage decreased to 3.0 V. FIG. 11 illustrates discharge capacities in batteries 24 to 33 obtained in a similar test.

[0058] Internal resistance was measured in batteries 15 to 23 and batteries 24 to 33 using an AC impedance technique (1 KHz). The results are shown in FIG. 12 and FIG. 13, respectively.

[0059] The results indicate that batteries including positive electrodes with a polymer content of 5 to 10 wt% in the layer of active material mixture and negative electrodes with a polymer content of 7 to 16 wt% in the layer of active material mixture can produce good performance. And, batteries including positive electrodes with a polymer content of 6 to 8 wt% in the layer of active material mixture and negative electrodes with a polymer content of 8 to 15 wt% in the layer of active material mixture can produce better performance. A battery with best performance is produced with the use of the positive electrode with a polymer content of 7 wt% and the negative electrode with a polymer content of 10 wt%.

[0060] As mentioned previously, the present invention can provide a polymer electrolyte battery affording a high current density by optimizing the porosity or polymer content or both in the layer of electrode active material.

[0061] Although the present invention has been described in terms of the presently preferred embodiments, it is to be understood that such disclosure is not to be interpreted as limiting. Various alterations and modifications will no doubt become apparent to those skilled in the art to which the present invention pertains, after having read the above disclosure. Accordingly, it is intended that the appended claims be interpreted as covering all alterations and modifications as fall within the true spirit and scope of the invention.

Claims

1. A polymer electrolyte battery including:

a nonaqueous electrolyte,
positive and negative electrode films or sheets each of which comprises a porous current collector and a layer of active material mixture disposed on both surfaces of said porous current collector, said layer of active material mixture containing a polymer capable of absorbing and retaining said electrolyte, and
porous separator films of a polymer capable of absorbing and retaining said electrolyte, said electrolyte being retained in said positive and negative electrodes and said separators,
wherein said positive electrodes are unitary laminated on said negative electrode with said separator being placed on both surfaces of said negative electrode to form a unitary laminated battery element sheet, and
wherein said separator and said layer of active material mixture of said positive and negative electrodes have a porosity in a range of 30 to 60%.

2. The polymer electrolyte battery in accordance with claim 1, wherein the porosity of said layer of active material mixture is in a range of 30 to 60%.

ture is in a range of 35 to 55% for the positive electrode and in a range of 35 to 45% for the negative electrode.

3. A polymer electrolyte battery including:

a nonaqueous electrolyte,
positive electrode films or sheets which comprise a porous current collector and a layer of active material mixture containing a polymer and a lithiated transition metal oxide disposed on both surfaces of said porous current collector,
a negative electrode film or sheet which comprises a porous current collector and a layer of active material mixture containing a polymer and a carbon material capable of intercalating and deintercalating lithium upon charge and discharge disposed on both surfaces of said current collector, and
porous separator films of a polymer, each polymer being capable of absorbing and retaining said electrolyte, said electrolyte being retained in said positive and negative electrodes and said separators,
wherein said positive electrodes are unitary laminated on said negative electrode with said separator being placed on both surfaces of said negative electrode to form a unitary laminated battery element sheet, and
wherein said layer of active material mixture has a porosity in a range of 35 to 55% for said positive electrode and a porosity in a range of 35 to 45% for said negative electrode, and said separator has a porosity in a range of 50 to 55%.

4. The polymer electrolyte battery in accordance with claim 3, wherein said carbon material is mainly composed of spheric graphite with a mean particle size of 6 to 50 μm prepared by carbonizing and graphitizing a carbonaceous mesophase particle.

5. The polymer electrolyte battery in accordance with claim 4, wherein said spheric graphite has an interplanar spacing of 3.365 to 3.390 angstroms and a crystal size of 200 to 650 angstroms along the c axis by X-ray diffractometry, and the I_{1360}/I_{1580} ratio of the peak intensity I_{1360} at 1360 cm^{-1} to the peak intensity I_{1580} at 1580 cm^{-1} by argon laser-Raman spectrometry is in a range of 0.20 to 0.40.

6. A polymer electrolyte battery comprising a nonaqueous electrolyte, positive and negative electrode films or sheets whose porous current collector has a layer of active material mixture containing a polymer on both surfaces, and porous separators of a polymer, each polymer being capable of absorbing and retaining said electrolyte, said electrolyte being retained in said positive and negative electrodes and said separators, wherein said positive electrodes are opposed to said negative electrode with said separator being placed on both surfaces of said negative electrode to form a unitary laminated battery element sheet, and wherein said layer of active material mixture contains said polymer in a range of 5 to 10 wt% for said positive electrode and in a range of 7 to 16 wt% for said negative electrode.

7. The polymer electrolyte battery in accordance with claim 6, wherein said layer of active material mixture contains said polymer in a range of 6 to 8 wt% for said positive electrode and in a range of 8 to 15 wt% for said negative electrode.

8. A polymer electrolyte battery including:

a nonaqueous electrolyte,
positive electrode films or sheets which comprise a porous current collector and a layer of active material mixture containing a polymer and a lithiated transition metal oxide disposed on both surfaces of said porous current collector,
a negative electrode film or sheet which comprises a porous current collector and a layer of active material mixture containing a polymer and a carbon material capable of intercalating and deintercalating lithium upon charge and discharge disposed on both surfaces of said current collector, and
porous separator films of a polymer, each polymer being capable of absorbing and retaining said electrolyte, said electrolyte being retained in said positive and negative electrodes and said separators,
wherein said positive electrodes are unitary laminated on said negative electrode with said separator being placed on both surfaces of said negative electrode to form a unitary laminated battery element sheet, and
wherein said layer of active material mixture contains said polymer in a range of 6 to 8 wt% for said positive electrode and in a range of 8 to 15 wt% for said negative electrode.

9. The polymer electrolyte battery in accordance with claim 8, wherein said carbon material is mainly composed of

spheric graphite with a mean particle size of 6 to 50 μm prepared by carbonizing and graphitizing a carbonaceous mesophase particle.

10. The polymer electrolyte battery in accordance with claim 9, wherein said spheric graphite has an interplanar spacing of 3.365 to 3.390 angstroms and a crystal size of 200 to 650 angstroms along the c axis by X-ray diffractometry, and the I_{1360}/I_{1580} ratio of the peak intensity I_{1360} at 1360 cm^{-1} to the peak intensity I_{1580} at 1580 cm^{-1} by argon laser-Raman spectrometry is in a range of 0.20 to 0.40.

11. A polymer electrolyte battery comprising a nonaqueous electrolyte, positive and negative electrode films or sheets whose porous current collector has a layer of active material mixture containing a polymer on both surfaces, and porous separators of a polymer, each polymer being capable of absorbing and retaining said electrolyte, said electrolyte being retained in said positive and negative electrodes and said separators, wherein said positive electrodes are opposed to said negative electrode with said separator being placed on both surfaces of said negative electrode to form a unitary laminated battery element sheet, and wherein said polymer contained in said layer of active material mixture is in a range of 5 to 10 wt% for said positive electrode and in a range of 7 to 16 wt% for said negative electrodes, and porosity of said layer of active material mixture is in a range of 35 to 55% for both electrodes.

12. The polymer electrolyte battery in accordance with claim 11, wherein the porosity and polymer content in said layer of active material mixture are in a range of 35 to 55% and 6 to 9 wt% for the positive electrode and in a range of 35 to 45% and 8 to 15 wt% for the negative electrode, respectively.

13. A polymer electrolyte battery including:

a nonaqueous electrolyte,

positive electrode films or sheets which comprise a porous current collector and a layer of active material mixture containing a polymer and a lithiated transition metal oxide disposed on both surfaces of said porous current collector,

a negative electrode film or sheet which comprises a porous current collector and a layer of active material mixture containing a polymer and a carbon material capable of intercalating and deintercalating lithium upon charge and discharge disposed on both surfaces of said current collector, and

porous separator films of a polymer, each polymer being capable of absorbing and retaining said electrolyte, said electrolyte being retained in said positive and negative electrodes and said separators,

wherein said positive electrodes are unitary laminated on said negative electrode with said separator being placed on both surfaces of said negative electrode to form a unitary laminated battery element sheet, and

wherein said layer of active material mixture of said positive electrode has a porosity of 35 to 55% and contains said polymer in a range of 6 to 8 wt%, and said layer of active material mixture of said negative electrode has a porosity of 35 to 45% and contains said polymer in a range of 8 to 15 wt%.

14. The polymer electrolyte battery in accordance with claim 13, wherein said carbon material is mainly composed of spheric graphite with a mean particle size of 6 to 50 μm prepared by carbonizing and graphitizing a carbonaceous mesophase particle.

15. The polymer electrolyte battery in accordance with claim 14, wherein said spheric graphite has an interplanar spacing of 3.365 to 3.390 angstroms and a crystal size of 200 to 650 angstroms along the c axis by X-ray diffractometry, and the I_{1360}/I_{1580} ratio of the peak intensity I_{1360} at 1360 cm^{-1} to the peak intensity I_{1580} at 1580 cm^{-1} by argon laser-Raman spectrometry is in a range of 0.20 to 0.40.

FIG. 1

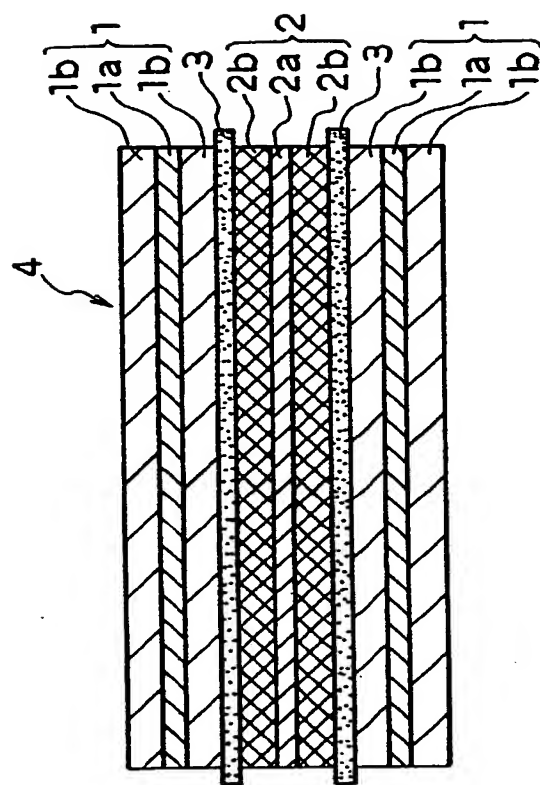
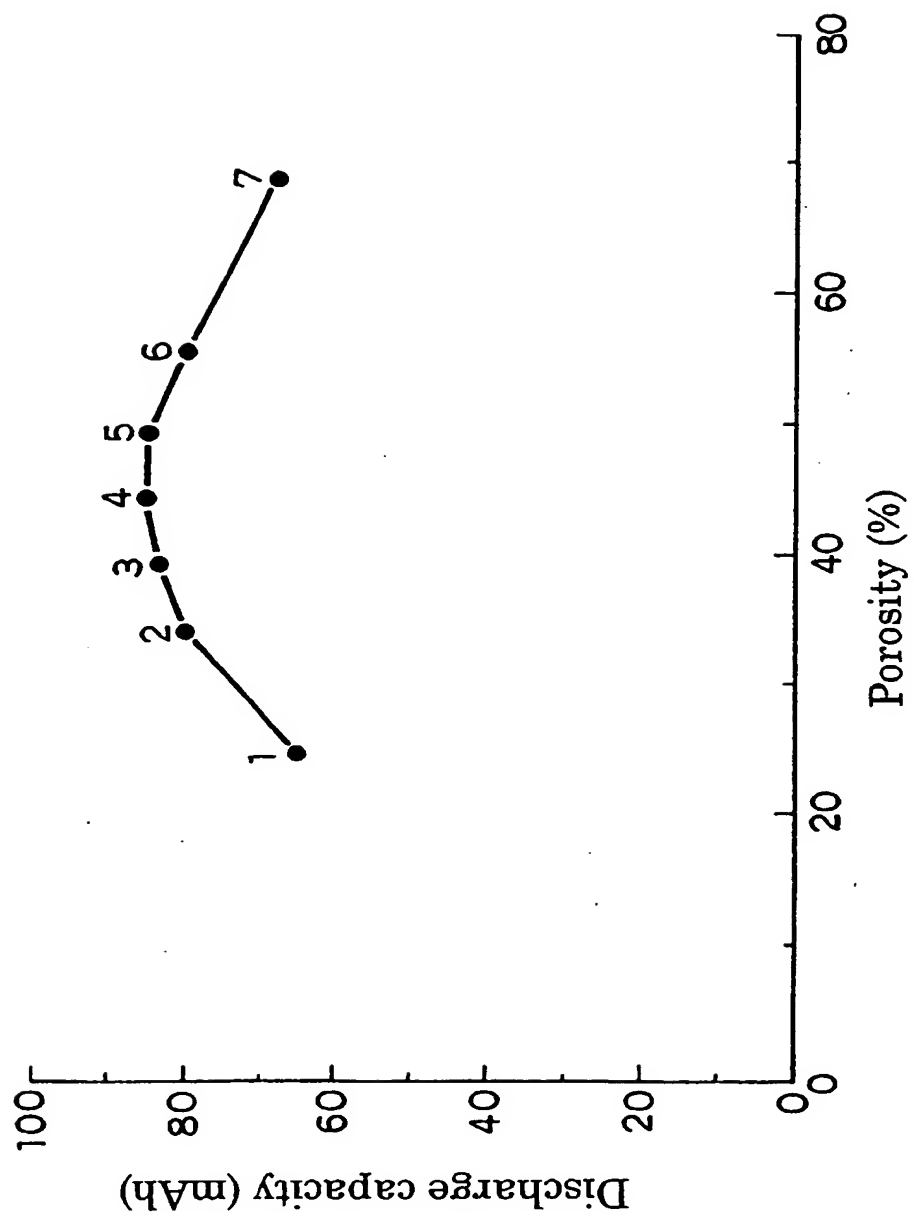
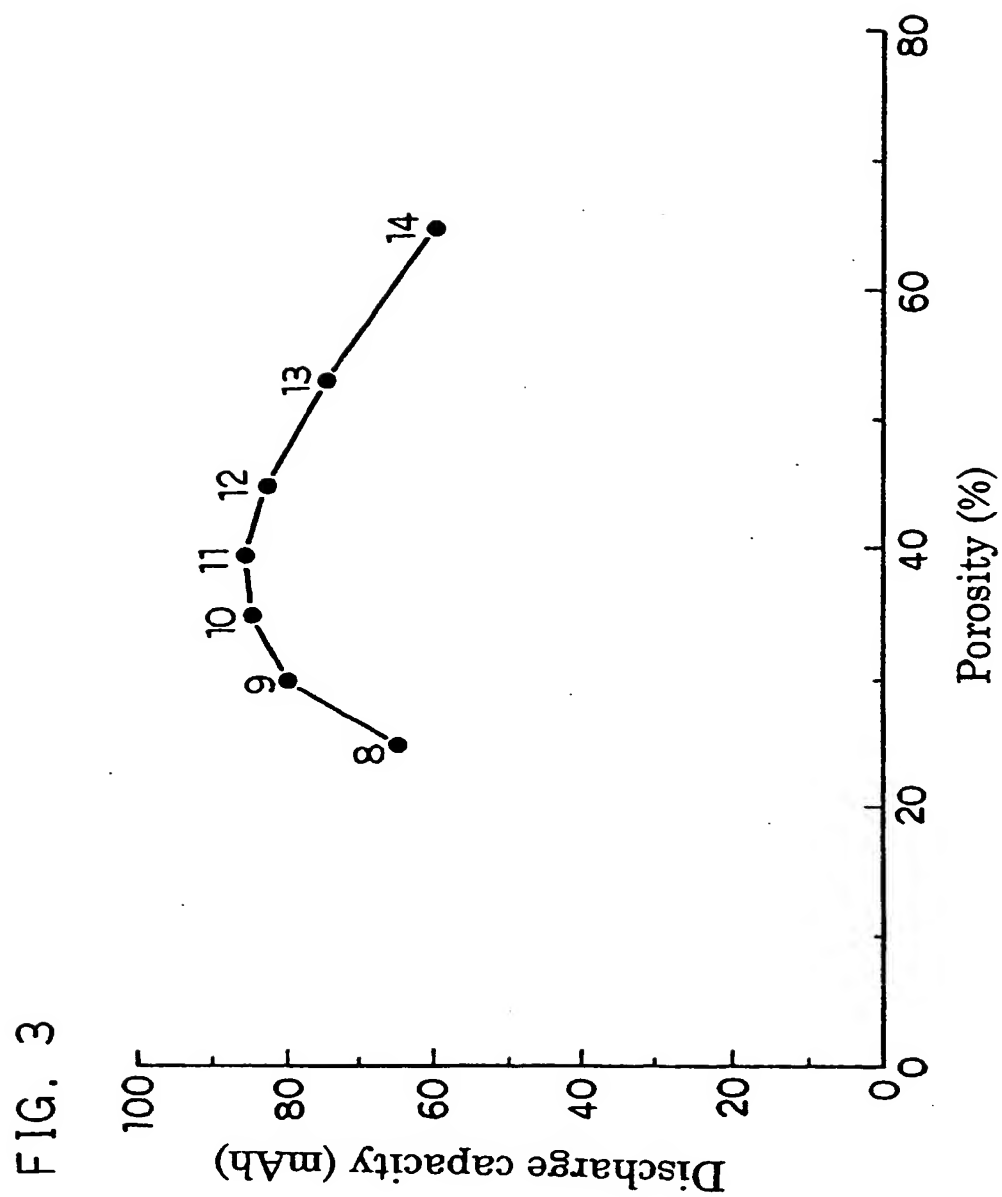
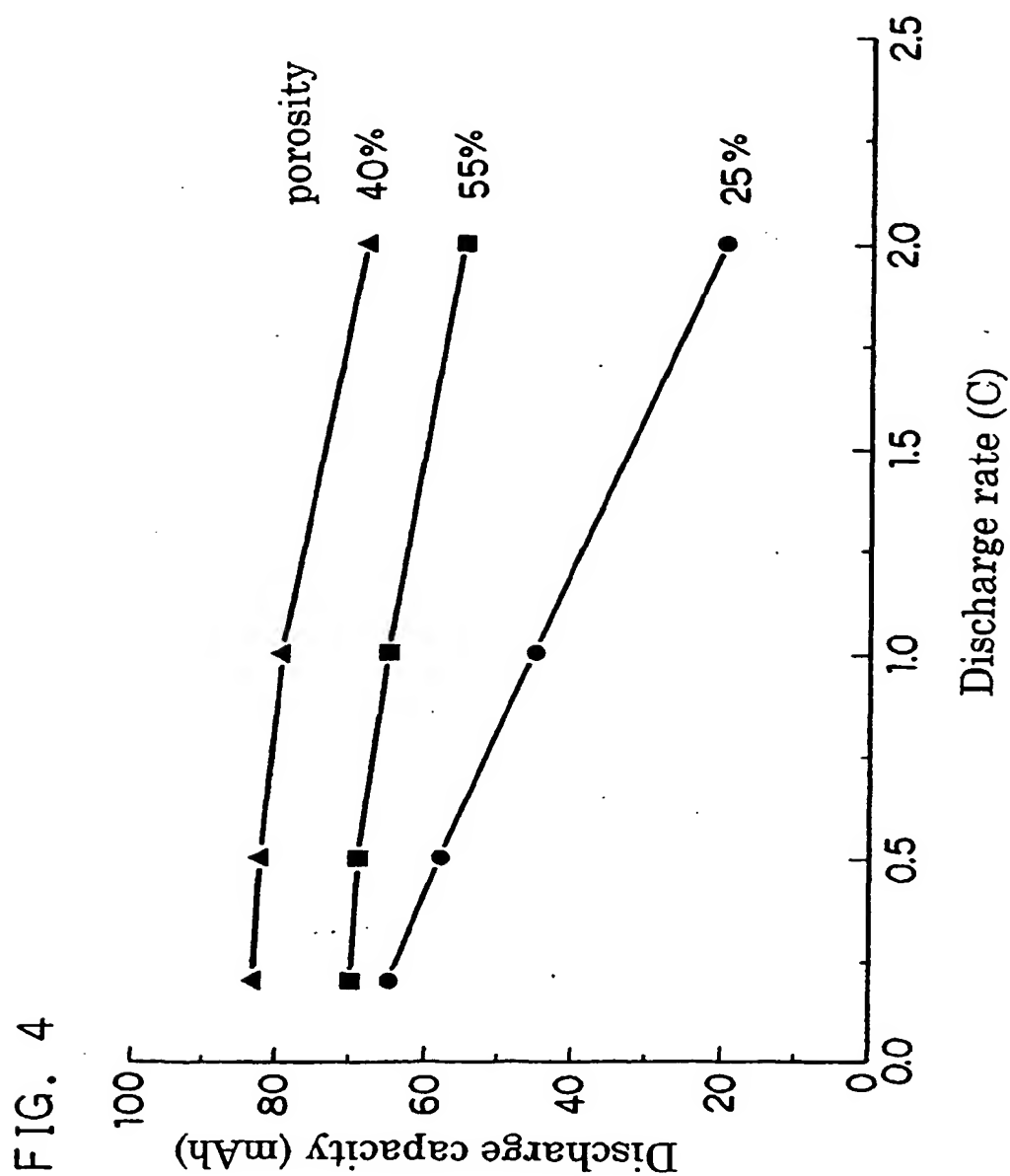
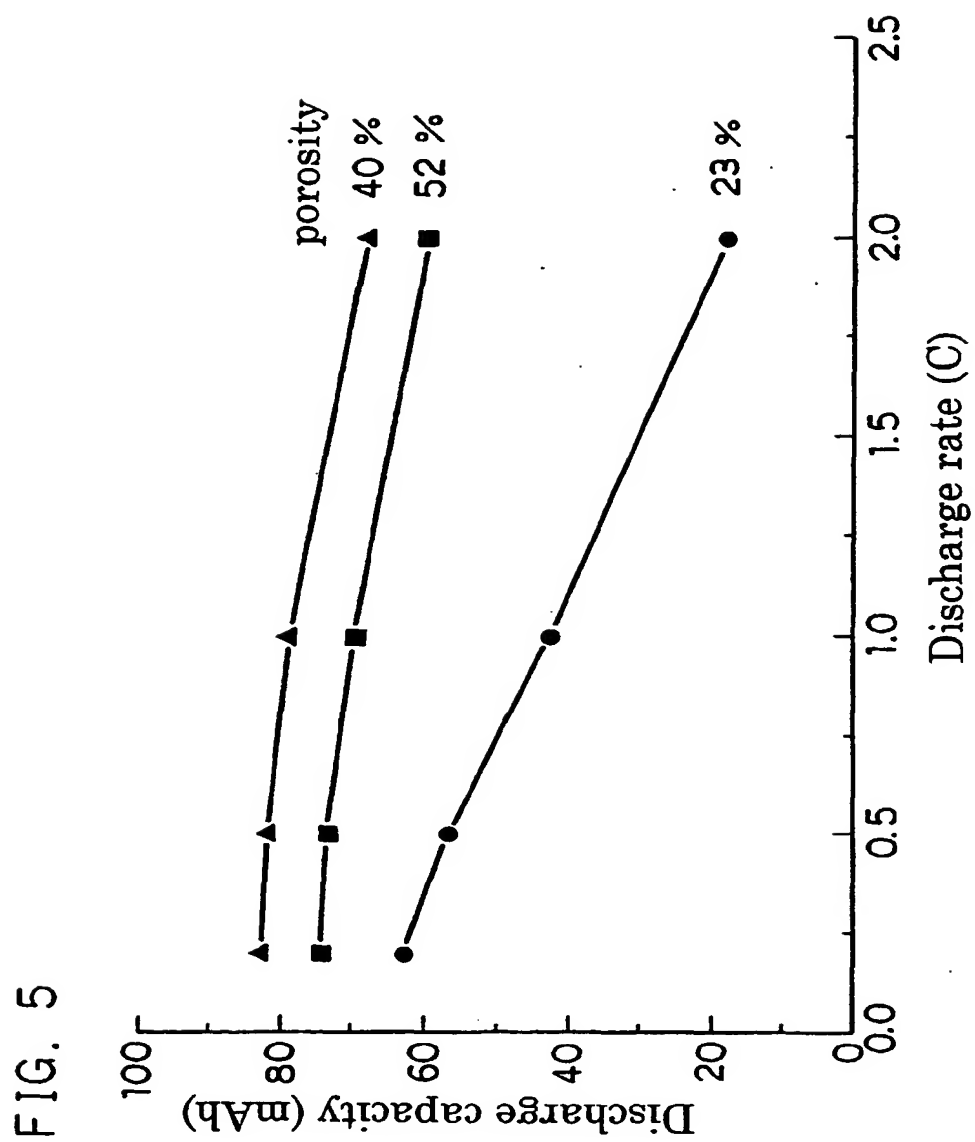


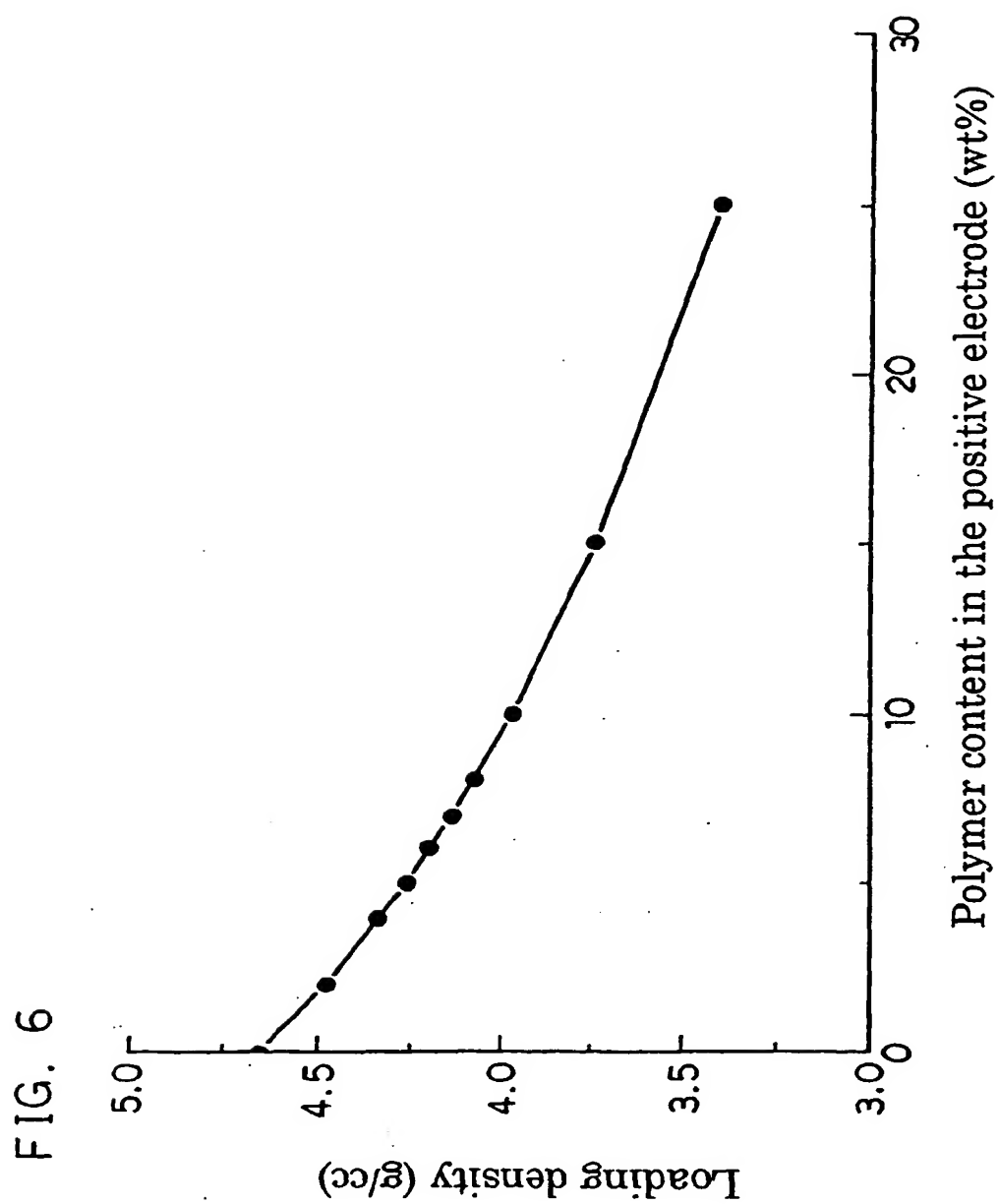
FIG. 2

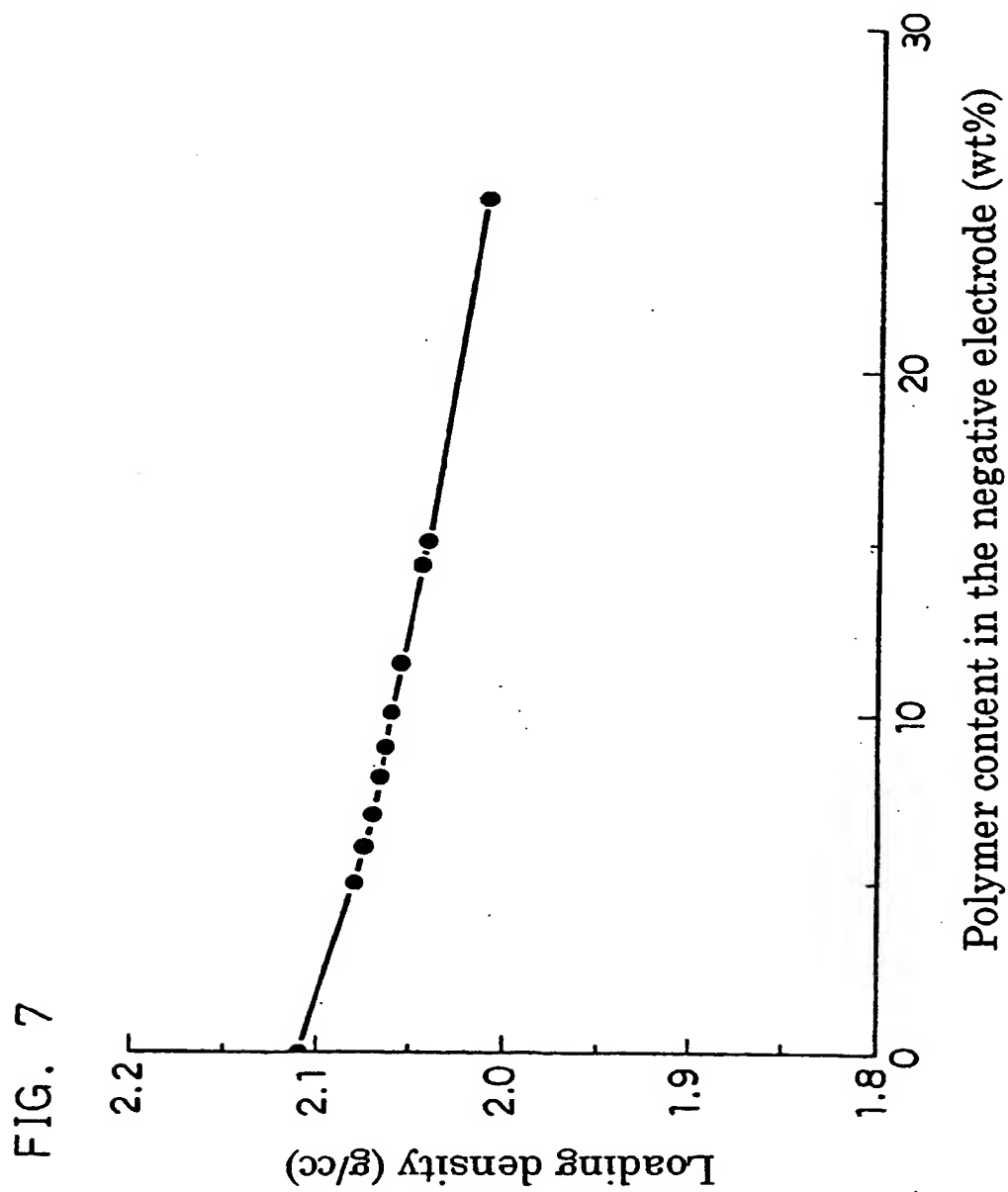


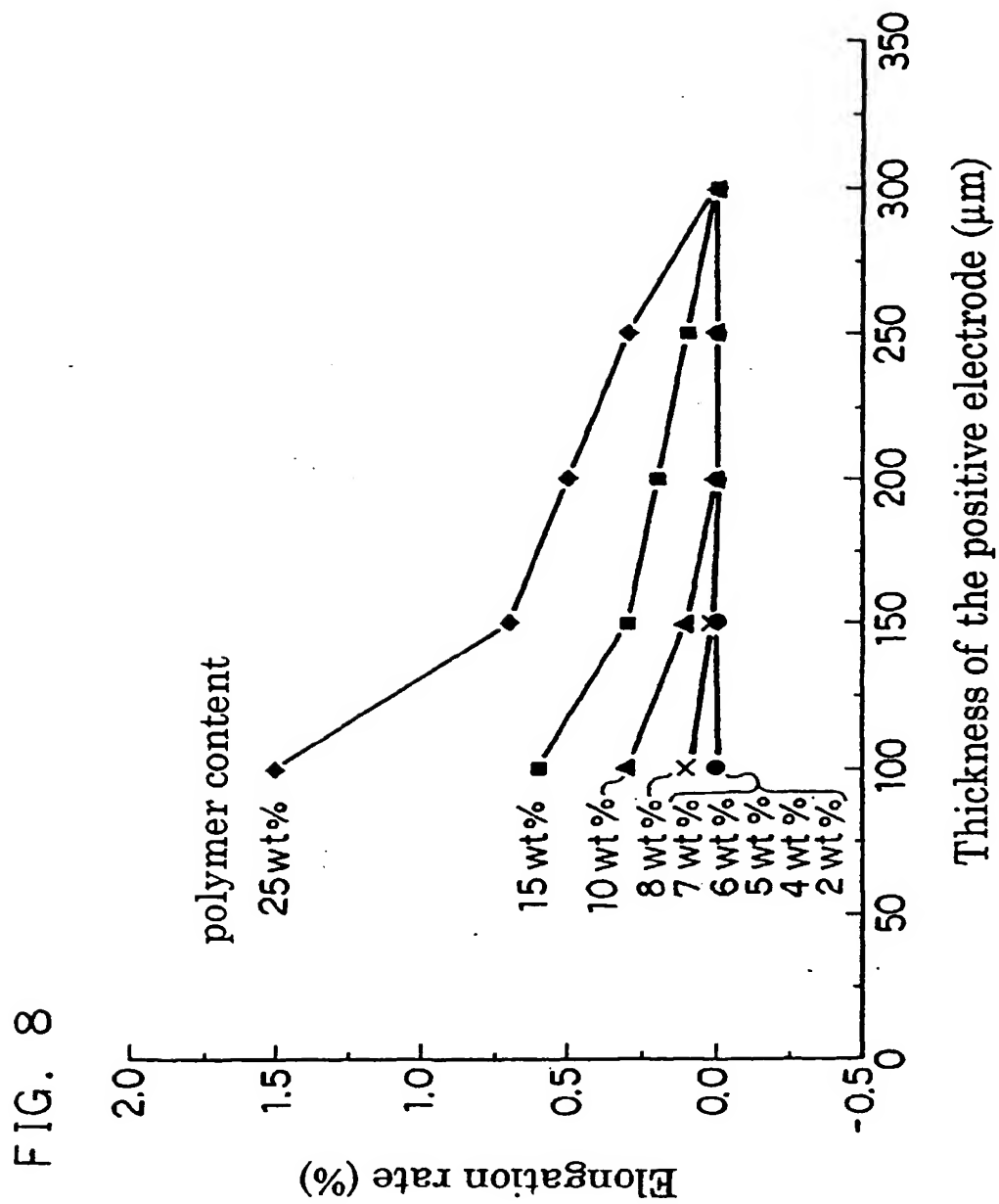


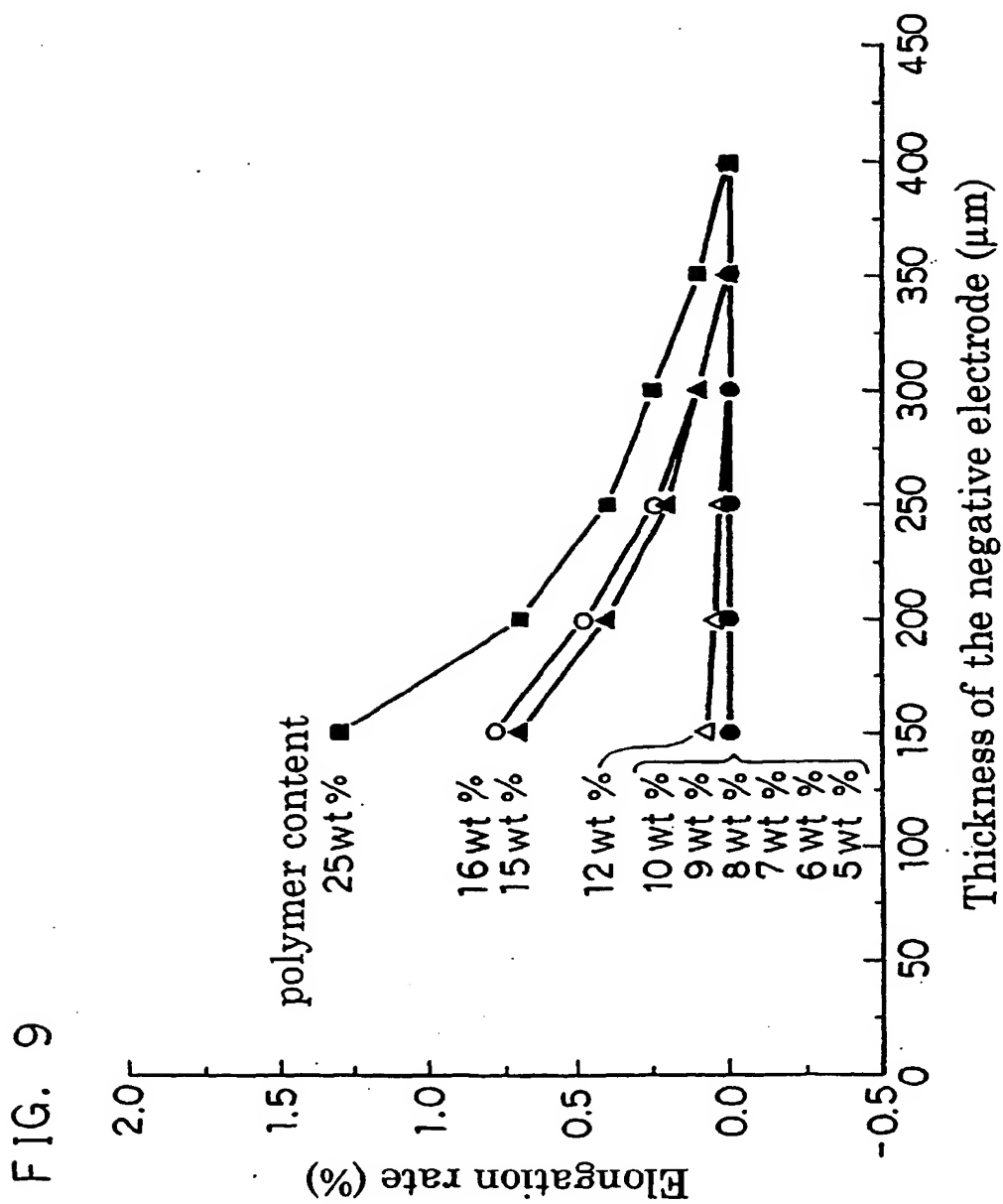












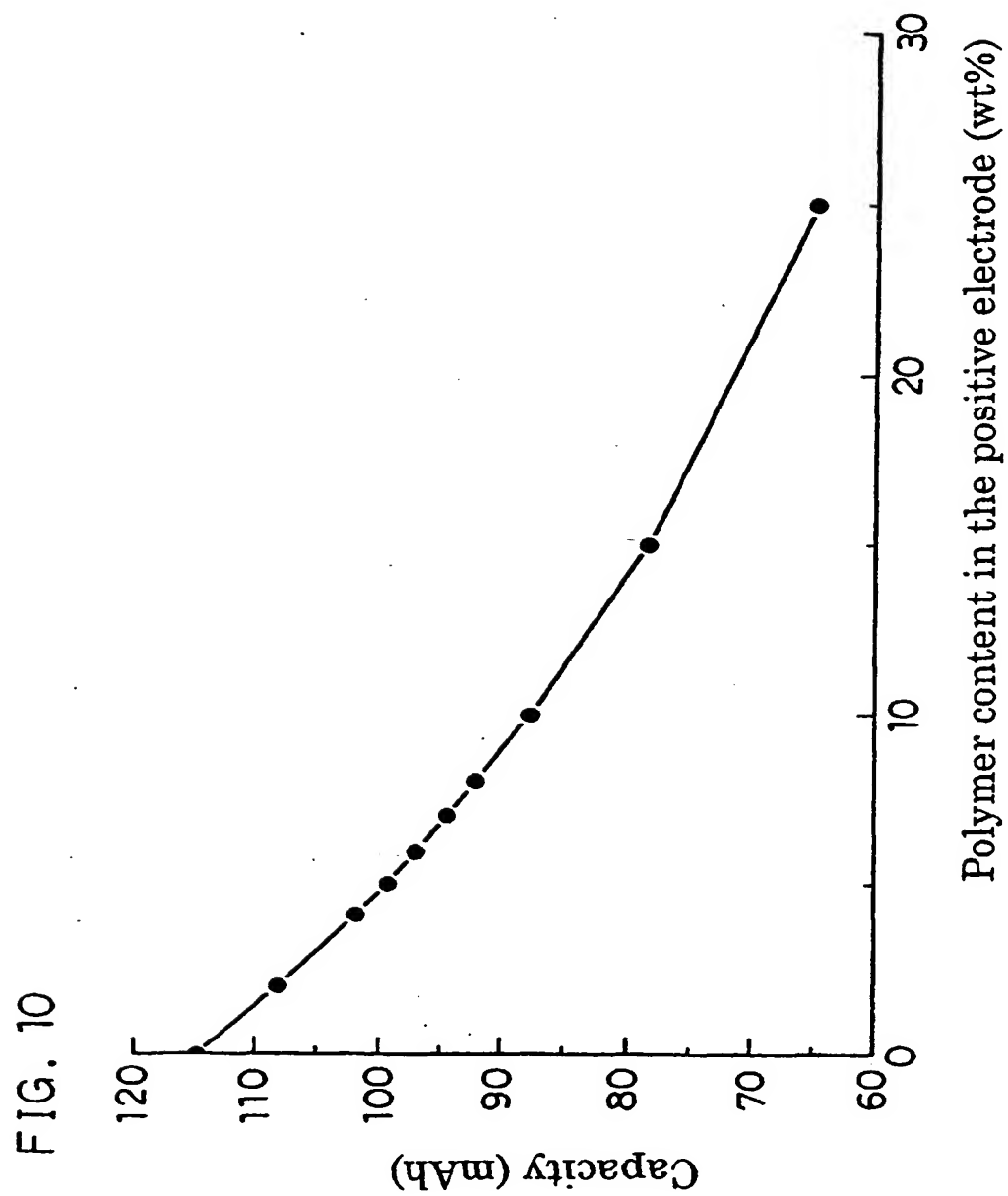


FIG. 11

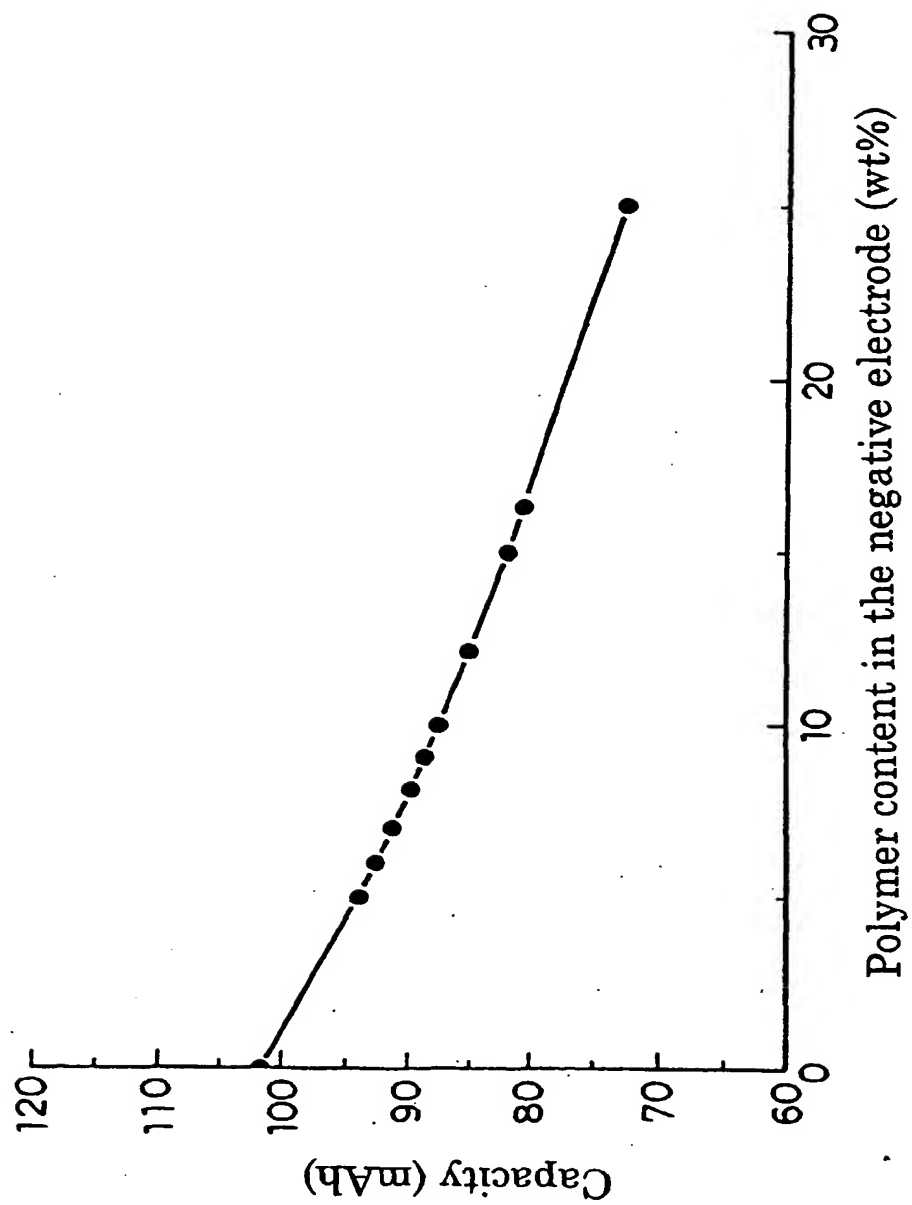


FIG. 12

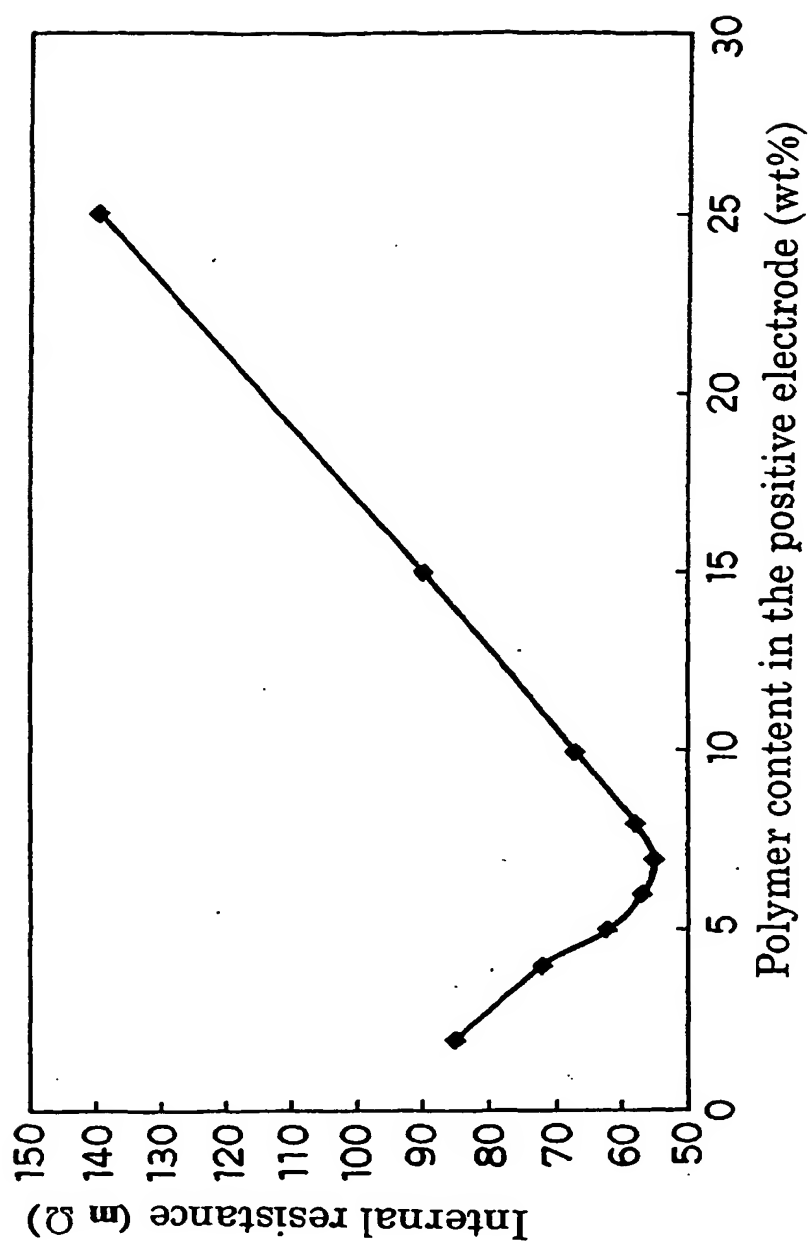
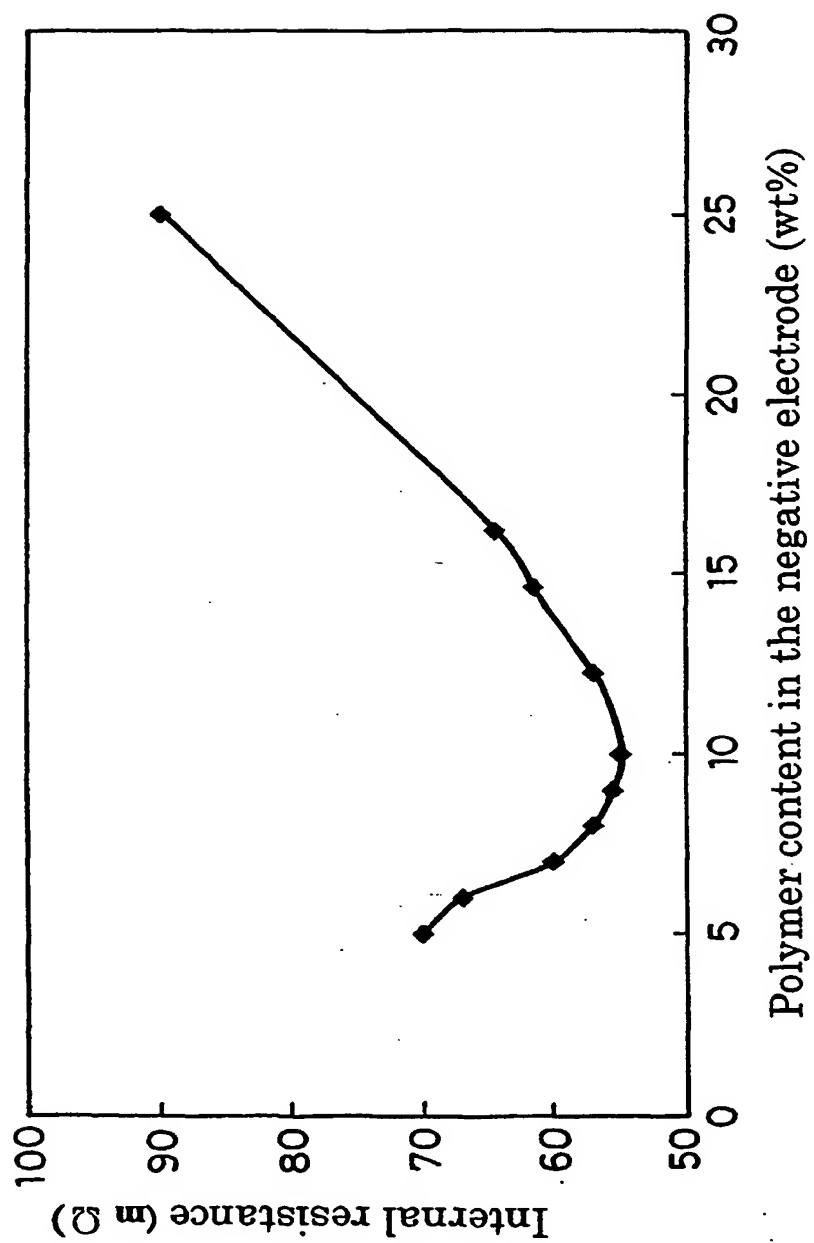
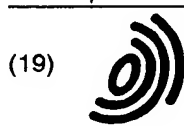


FIG. 13





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Hirakata-shi, Osaka 573-0106 (JP)

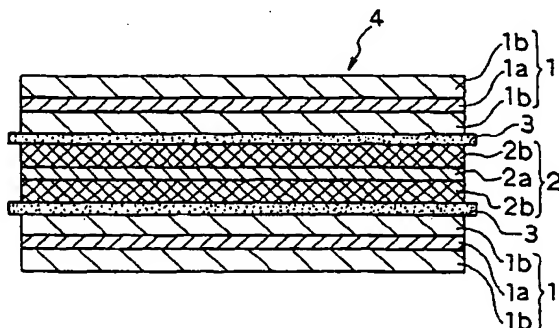
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(54) **Polymer electrolyte battery**

(57) Disclosed is a polymer electrolyte battery affording a high capacity density in which a layer of electrode active material mixture containing a polymer has an adequately regulated porosity and/or polymer content. The battery includes a unitary laminated battery sheet composed of a negative electrode combined with positive electrodes, with a porous polymer separator being placed on both surfaces of the negative electrode.

Each of the electrodes comprises a current collector and a layer of active material mixture disposed on both surfaces of the current collector, and the polymer is capable of absorbing and retaining nonaqueous electrolyte. The separator and the layer of electrode active material mixture have a porosity of 30 to 60%. Preferable polymer contents in the layer of active material mixture are in a range of 5 to 10 wt% for the positive electrode and in a range of 7 to 16 wt% for the negative electrode.

FIG. 1





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EUROPEAN SEARCH REPORT

Application Number
EP 99 10 1702

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 803 925 A (JAPAN STORAGE BATTERY CO LTD) 29 October 1997 (1997-10-29) * column 5, line 22 - column 6, line 59 * * column 8, line 1 - column 11, line 12; claims 1-18 *	1,3,6	H01M10/40 H01M4/58 H01M6/40
X	EP 0 730 316 A (ATOCHEM NORTH AMERICA ELF) 4 September 1996 (1996-09-04) * page 5, line 17 - page 7, line 39 * * page 13, line 35-50; claims 1-16 *	1	
Y	US 5 587 253 A (WARREN PAUL C ET AL) 24 December 1996 (1996-12-24) * column 4, line 33 - column 7, line 31; claims 1-12; figure 4 *	1-5	
A		6-8, 11-13	
Y	US 5 456 000 A (TARASCON JEAN-MARIE ET AL) 10 October 1995 (1995-10-10) * column 5, line 64 - column 9, line 45 * * claims 1-23 *	1-3	
A		6-8, 11-13	
Y	US 5 344 724 A (OZAKI YOSHIYUKI ET AL) 6 September 1994 (1994-09-06) * column 3, line 49 - column 4, line 46 * * column 6, line 43 - column 7, line 59 * * column 12, line 60 - column 14, line 62 *	4,5	H01M
A		9,10,14, 15	
X	WO 97 43795 A (MOTOROLA INC) 20 November 1997 (1997-11-20) * page 3, line 26 - page 8, line 27; claims 1-12 *	1	
A		2,3,6-8, 11-13	
		-/--	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 February 2003	Examiner De Vos, L
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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Application Number
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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet 8

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 10 1702

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.6)
X	US 5 540 741 A (TARASCON JEAN-MARIE ET AL) 30 July 1996 (1996-07-30) * column 10, line 21 - column 14, line 38; claims 1-26 *	1	
D, P, X	--- PATENT ABSTRACTS OF JAPAN vol. 1998, no. 12, 31 October 1998 (1998-10-31) & JP 10 189053 A (TOSHIBA BATTERY CO LTD), 21 July 1998 (1998-07-21) * abstract *	1	
E	--- WO 99 19924 A (MINNESOTA MINING & MFG) 22 April 1999 (1999-04-22) * page 10, line 2 - page 12, line 1 * * page 34, line 5 - page 37, line 21 * * page 42, line 9 - page 52, line 13 * * claims 1-14 *	1,6	
A	--- US 4 853 305 A (ANDERMAN MENAHEM ET AL) 1 August 1989 (1989-08-01) * column 5, line 35 - column 8, line 41 * * column 10, line 10 - column 11, line 25; claims 1-29 * * column 9, line 51 - column 11, line 25 *	1-3,6-8, 11-13	
A	--- US 4 731 310 A (MENAHEM ANDERMAN) 15 March 1988 (1988-03-15) * column 4, line 15-35; claims 1-16 *	6,7	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 February 2003	Examiner De Vos, L
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

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European Patent
Office

LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 99 10 1702

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-5

Laminar polymer electrolyte battery with porous electrode collectors covered on both surfaces with active material layers containing a polymer, with central negative electrode and porous filmlike separator characterized by the porosity of the separator and of the active material layers being in the range of 30 to 60%. Specific graphitic material as anode.

2. Claims: 6-15

Laminar polymer electrolyte battery with porous electrode collector covered on both surfaces with active material mixture containing a polymer, with central negative electrode covered on both surfaces by a porous filmlike separator, said battery being characterized by the content of polymer in said active material mixtures (5 to 10 weight % for the positive electrode, 7 to 16% for the negative). Moreover the porosity of these layers of active material mixtures can be specified.

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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-02-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0803925 A	29-10-1997	JP 8195220 A	30-07-1996
		US 6027836 A	22-02-2000
		EP 0803925 A1	29-10-1997
EP 0730316 A	04-09-1996	CN 1137178 A	04-12-1996
		EP 0730316 A1	04-09-1996
		HU 9600516 A2	30-12-1996
		JP 8250127 A	27-09-1996
		SG 59922 A1	22-02-1999
		US 5922493 A	13-07-1999
US 5587253 A	24-12-1996	US 5460904 A	24-10-1995
		US 5418091 A	23-05-1995
		US 5296318 A	22-03-1994
		AU 700453 B2	07-01-1999
		AU 6457196 A	05-03-1997
		CA 2228222 A1	20-02-1997
		EP 0842547 A1	20-05-1998
		IL 118907 A	31-01-2000
		JP 10510669 T	13-10-1998
		JP 3164586 B2	08-05-2001
		WO 9706569 A1	20-02-1997
		CA 2177361 A1	08-06-1995
		DE 737369 T1	13-02-1997
		EP 0737369 A1	16-10-1996
		IL 111559 A	05-04-1998
		JP 2967127 B2	25-10-1999
		JP 9500485 T	14-01-1997
		WO 9515589 A1	08-06-1995
		US 5478668 A	26-12-1995
		US 5456000 A	10-10-1995
		US 5540741 A	30-07-1996
		US 5470357 A	28-11-1995
		US 5571634 A	05-11-1996
		CA 2168433 A1	02-03-1995
		DE 714561 T1	24-10-1996
		EP 0714561 A1	05-06-1996
		JP 3253090 B2	04-02-2002
		JP 8509100 T	24-09-1996
		WO 9506332 A1	02-03-1995
		US 5429891 A	04-07-1995
		US 5607485 A	04-03-1997
		CA 2157012 A1	15-09-1994
		EP 0699348 A1	06-03-1996
		JP 2853096 B2	03-02-1999
		JP 8507407 T	06-08-1996

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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ON EUROPEAN PATENT APPLICATION NO.**

EP 99 10 1702

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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-02-2003

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5587253	A		WO	9420996 A1	15-09-1994
US 5456000	A	10-10-1995	US	5460904 A	24-10-1995
			US	5418091 A	23-05-1995
			US	5296318 A	22-03-1994
			CA	2177361 A1	08-06-1995
			DE	737369 T1	13-02-1997
			EP	0737369 A1	16-10-1996
			IL	111559 A	05-04-1998
			JP	2967127 B2	25-10-1999
			JP	9500485 T	14-01-1997
			WO	9515589 A1	08-06-1995
			US	5478668 A	26-12-1995
			US	5540741 A	30-07-1996
			US	5470357 A	28-11-1995
			US	5587253 A	24-12-1996
			US	5571634 A	05-11-1996
			CA	2168433 A1	02-03-1995
			DE	714561 T1	24-10-1996
			EP	0714561 A1	05-06-1996
			JP	3253090 B2	04-02-2002
			JP	8509100 T	24-09-1996
			WO	9506332 A1	02-03-1995
			US	5429891 A	04-07-1995
			US	5607485 A	04-03-1997
			CA	2157012 A1	15-09-1994
			EP	0699348 A1	06-03-1996
			JP	2853096 B2	03-02-1999
			JP	8507407 T	06-08-1996
			WO	9420996 A1	15-09-1994
US 5344724	A	06-09-1994	JP	3191394 B2	23-07-2001
			JP	5290833 A	05-11-1993
WO 9743795	A	20-11-1997	US	5688293 A	18-11-1997
			WO	9743795 A1	20-11-1997
US 5540741	A	30-07-1996	US	5460904 A	24-10-1995
			US	5418091 A	23-05-1995
			US	5296318 A	22-03-1994
			CA	2177361 A1	08-06-1995
			DE	737369 T1	13-02-1997
			EP	0737369 A1	16-10-1996
			IL	111559 A	05-04-1998
			JP	2967127 B2	25-10-1999
			JP	9500485 T	14-01-1997

EPO FORM P0459

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 10 1702

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24-02-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5540741 A		WO 9515589 A1	08-06-1995
		US 5478668 A	26-12-1995
		US 5456000 A	10-10-1995
		US 5470357 A	28-11-1995
		US 5587253 A	24-12-1996
		US 5571634 A	05-11-1996
		CA 2168433 A1	02-03-1995
		DE 714561 T1	24-10-1996
		EP 0714561 A1	05-06-1996
		JP 3253090 B2	04-02-2002
		JP 8509100 T	24-09-1996
		WO 9506332 A1	02-03-1995
		US 5429891 A	04-07-1995
		US 5607485 A	04-03-1997
		CA 2157012 A1	15-09-1994
		EP 0699348 A1	06-03-1996
		JP 2853096 B2	03-02-1999
		JP 8507407 T	06-08-1996
		WO 9420996 A1	15-09-1994
JP 10189053 A	21-07-1998	NONE	
WO 9919924 A	22-04-1999	US 6171723 B1	09-01-2001
		AU 6329398 A	03-05-1999
		JP 2001520443 T	30-10-2001
		WO 9919924 A1	22-04-1999
		US 6143216 A	07-11-2000
US 4853305 A	01-08-1989	AT 99836 T	15-01-1994
		AU 605140 B2	10-01-1991
		AU 7057087 A	01-10-1987
		BR 8701306 A	29-12-1987
		CA 1278033 A1	18-12-1990
		DE 3788671 D1	17-02-1994
		DE 3788671 T2	28-04-1994
		EP 0243653 A2	04-11-1987
		ES 2048727 T3	01-04-1994
		HK 1008121 A1	30-04-1999
		IL 81959 A	10-06-1990
		JP 2750350 B2	13-05-1998
		JP 63250055 A	17-10-1988
		JP 2986431 B2	06-12-1999
		JP 10083839 A	31-03-1998
		KR 9601145 B1	19-01-1996
		US 5143805 A	01-09-1992

EPO FORM P0459

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 10 1702

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-02-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4731310 A	15-03-1988	AT 99836 T	15-01-1994
		AU 605140 B2	10-01-1991
		AU 7057087 A	01-10-1987
		BR 8701306 A	29-12-1987
		CA 1278034 A1	18-12-1990
		DE 3788671 D1	17-02-1994
		DE 3788671 T2	28-04-1994
		EP 0243653 A2	04-11-1987
		ES 2048727 T3	01-04-1994
		HK 1008121 A1	30-04-1999
		IL 81959 A	10-06-1990
		JP 2750350 B2	13-05-1998
		JP 63250055 A	17-10-1988
		JP 2986431 B2	06-12-1999
		JP 10083839 A	31-03-1998
		KR 9601145 B1	19-01-1996

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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